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SYNTHESIS OF ALLYLSILANES AND β-(TRIMETHYLSILYL)KETONES VIA LITHIUM 1-ALKYNYLTRIALKYLBORATES

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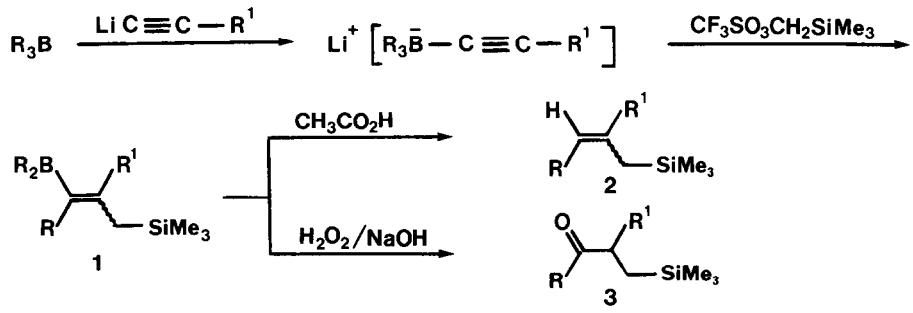
Abstract: Allylsilanes or β-(trimethylsilyl)ketones were prepared by treating lithium 1-alkynyltrialkylborates with (trimethylsilyl)methyl trifluoromethanesulfonate followed by protonolysis or oxidation, respectively.

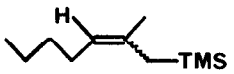
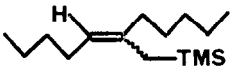
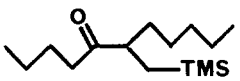
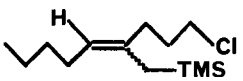
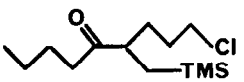
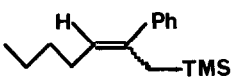
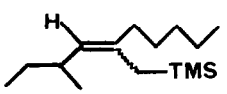
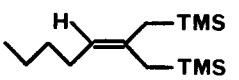
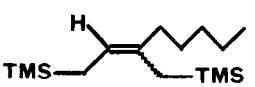
Recent developments in organoborane and organosilane chemistry have provided organic chemists with many new tools for chemical transformations. It is also becoming increasingly evident that their applications could be further expanded by coupling these two sets of reactions together.[1] As part of our continuing efforts in synthesizing reagents for such purpose, we now report a simple route to compounds containing both boron and silicon appendages and their subsequent transformations.

It has been shown that electrophilic attack of lithium 1-alkynyltrialkylborates by alkylating agents can induce migration of an alkyl group from the boron atom to the adjacent acetylenic carbon atom to afford alkenyldialkylboranes.[2] We found that by simply using (trimethylsilyl)methyl trifluoromethanesulfonate[3] as the inducing electrophile, intermediate 1 having both alkenylborane and allylsilane moieties could be easily prepared. Subsequent protonolysis or oxidation provided the corresponding allylsilane or β-(trimethylsilyl)ketone, respectively (Table I).[4]



Allyllsilanes have found many new synthetic applications.[7] Conjugate addition to α,β-unsaturated ketones (Sakurai reaction) took place smoothly in the presence of a Lewis acid.[8] Allylsilane 2c substituted with alkyl chloride side chain could thus be utilized as a "donor-

Table I. Synthesis of Allylsilanes and β-(Trimethylsilyl)ketones

R_3B	Alkyne	product[a]		isolated yield,%	isomer ratio[b]
n-Bu_3B	propyne	2a		80	Z:E=3:2[c]
n-Bu_3B	1-heptyne	2b		72	2.5:1
n-Bu_3B	1-heptyne	3b		59	-
n-Bu_3B	5-chloro-1-pentyne	2c		81	2.5:1
n-Bu_3B	5-chloro-1-pentyne	3c		74	-
n-Bu_3B	phenylacetylene	2d		72	Z:E=4:1[d]
s-Bu_3B	1-heptyne	2e		53	2.5:1
n-Bu_3B	$HC{\equiv}CCH_2SiMe_3$	2f		79	-
$(Me_3SiCH_2)_3B$	1-heptyne	2g		45	3.5:1

[a] The isolated products have been fully characterized by IR and ^1H and ^{13}C NMR spectroscopy (270 MHz, $CHCl_3$ at δ 7.26 for ^1H and $CDCl_3$ at δ 77.02 for ^{13}C as internal reference) and satisfactory elemental composition by combustion analysis (C and H) and/or mass spectroscopy. [b] The isomer ratio was determined by integration of the ^1H NMR spectrum. [c] The assignment of the geometry is based on the comparison of the ^{13}C NMR spectrum with the reported data.[5] [d] The assignment of the geometry is based on the comparison of the chemical shifts of the vinylic protons with those of the E and the Z isomers of 3-phenyl-3-hexene.[6]

acceptor" conjuctive reagent for the construction of carbocyclic structures with an initial Sakurai reaction followed by an intramolecular alkylation reaction.[9] Compound 2f prepared from 3-(trimethylsilyl)-1-propyne[10] contains two allylsilane moieties and thus could serve as a "donor-donor" conjunctive reagent. Only a few synthetic methods have been reported for such compounds.[11] Intermediate 1g bearing three reactive sites was prepared and isolated from tris[(trimethylsilyl)methyl]borane.[12] It is very resistant to hydrolysis by acetic acid

and to oxidation by alkaline hydrogen peroxide, presumably due to the steric bulk surrounding the boron atom. However, prolonged heating (18h) with acetic acid at reflux temperature of THF eventually produced 2g, a group of compounds receiving increasing attention.[13]

The lack of stereoselectivity in the migration step resulted in the formation of mixtures of the E and the Z isomers of allylsilanes. We are currently investigating the use of other ligands on the boron atom for improvement. Significant enhance of the stereoselectivity has been observed previously in the alkylation of lithium thexyldialkylalkynylborates.[14]

It has been demonstrated that β-(trimethylsilyl)ketones can be brominated and desilylbrominated specifically to α,β-unsaturated ketones under mild conditions.[15] The synthetic route to compound 3 thus provides a regioselective pathway to a variety of masked α,β-unsaturated ketones. By simply varying the starting organoborane and 1-alkyne, the site of the β-silyl substituent can be easily controlled. The lack of stereoselectivity in the migration step is inconsequential, since the stereochemistry of the double bond is lost in the following oxidative workup.

The following procedure for the preparation of 2c is representative. To a 50-mL round-bottomed flask purged with nitrogen were introduced with syringes 1.06 mL of 5-chloro-1-pentyne (1.098 g, 10.7 mmol) and 10 mL of THF. The reaction flask was cooled to 0°C and then charged with 4.59 mL of n-butyllithium (2.33 M in hexane, 10.7 mmol) followed by 10.7 mL of 1.0 M tri-n-butylborane (10.7 mmol) in THF. After 30 min of stirring, the reaction mixture was cooled to 0°C, treated with 2.2 mL of (trimethylsilyl)methyl triflate (2.5 g, 10.7 mmol), and stirred at room temperature for 4 hours. Protonolysis was carried out with 3 mL of glacial acetic acid at room temperature for 1 h. After oxidative workup with 15 mL of 3N NaOH and 6 mL of 30% H_2O_2, the aqueous layer was separated and extracted twice with 10 mL of Et_2O. The combined organic layers were then washed with water, dried over $MgSO_4$, and concentrated. Column chromatography on silica gel (elution with petroleum ether) gave 2.740 g (81%) of 2c as a colorless liquid: IR (neat) 1655 (w), 1440 (m), 1250 (s), 1160 (m), 850 (s), 730 (m), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.00 (1H, m), 3.49 (2H, t, J=6.6 Hz), 2.1-1.8 (6H, m), 1.47 (CH_2Si of the major isomer, s), 1.41 (CH_2Si of the minor isomer, s), 1.35-1.25 (4H, m), 0.87 (3H, t), 0.00 (Me_3Si of the major isomer, s), -0.02 (Me_3Si of the minor isomer, s); ^{13}C NMR ($CDCl_3$) δ (major set) 134.92, 123.15, 44.76, 36.17, 32.25, 31.19, 28.22, 22.55, 21.19, 14.10, -0.60; (minor set) 134.84, 124.65, 44.94, 32.67, 31.39, 29.33, 27.73, 26.66, 22.42, 14.06, -1.16; MS, m/e 246 (M^+), 189, 184, 73. Anal. Calcd for $C_{13}H_{27}ClSi$: C, 63.24; H, 11.02. Found: C, 63.07; H, 10.76.

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4. Spectral data for 2a, 3b, 3c, 2f, and 2g. 2a: ^{1}H NMR δ 5.00 [(Z)-CH=C, t, J=6.8 Hz], 4.94 [(E)-CH=C, t, J=7.1 Hz], 1.97 [(E)-CH_2C=C, q, J=6.6 Hz], 1.895 [(Z)-CH_2C=C, q, J=6.6 Hz], 1.665 [(Z)-CH_3C=C, s], 1.585 [(E)-CH_3C=C, s], 1.505 [(Z)-CH_2Si, s], 1.455 [(E)-CH_2Si, s], 1.30 (4H, m), 0.89 (3H, t), 0.025 [(Z)-Me_3Si, s], -0.002 [(E)-Me_3Si, s]; ^{13}C NMR δ (Z-isomer) 132.67, 122.56, 32.27, 28.29, 26.26, 23.22, 22.56, 14.08, -0.65; (E-isomer) 132.38, 122.91, 32.45, 29.88, 27.91, 22.38, 18.61, 14.04, -1.21; MS, m/e 184 (M^+), 169, 141, 127, 73. 3b: IR (neat) 1710 (s), 1460 (m), 1250 (s), 855 (s), 830 (s), 690 (m) cm^{-1}; ^{1}H NMR δ 2.53-2.44 (1H, m), 2.40 (1H, t, J=7 Hz), 2.395 (1H, t, J=7 Hz), 1.65-1.45 (3H, m), 1.4-1.15 (9H, m) 0.89 (3H, t), 0.86 (3H, t), 0.59 (1H, d, J=7.0 Hz), 0.54 (1H, d, J=7.1 Hz), -0.02 (9H, s); ^{13}C NMR δ 214.54, 48.12, 40.63, 34.36, 31.89, 27.09, 25.81, 22.47, 22.43, 18.75, 13.96, 13.86, -0.98; MS, m/e 256 (M^+), 241, 185, 171, 73. Anal. Calcd for $C_{15}H_{32}OSi$: C, 70.24; H, 12.57. Found: C, 70.42; H, 12.94. 3c: ^{1}H NMR δ 3.48 (2H, m), 2.56-2.46 (1H, m), 2.41 (2H, t), 1.75-1.45 (6H, m), 1.29 (2H, m), 0.89 (3H, t), 0.58 (1H, d, J=7.3 Hz), 0.53 (1H, d, J=7.3 Hz), -0.007 (9H, s); ^{13}C NMR δ 213.88, 47.36, 44.78, 40.61, 31.07, 30.26, 25.80, 22.41, 18.83, 13.87, -0.97; MS, m/e 247 (M^+-CH_3), 227, 220, 205, 185, 73. 2f: ^{1}H NMR 4.80 (1H, t, J=7 Hz), 1.90 (2H, q, J=7 Hz), 1.45 (2H, s), 1.38 (2H, s), 1.30 (4H, br), 0.89 (3H, t), 0.027 (9H, s), 0.003 (9H, s); ^{13}C NMR δ 133.75, 120.09, 32.64, 29.41, 28.48, 23.71, 22.47, 14.09, -0.61, -1.10; MS, m/e 256 (M^+), 241, 213, 200, 125, 112, 73. 2g: ^{1}H NMR δ 5.02 (HC=C of the major isomer, t, J=8.2 Hz), 4.96 (HC=C of the minor isomer, t, J=8.2 Hz), 1.92 (2H, t, J=7 Hz), 1.45 (2H, s), 1.42-1.2 (8H, m), 0.89 (3H, t), 0.023 and -0.011 (Me_3Si of the major isomer, s), 0.001 and -0.006 (Me_3Si of the minor isomer, s); ^{13}C NMR δ (major set) 135.01, 116.81, 39.30, 31.62, 28.34, 22.63, 20.57, 18.78, 14.16, -0.49, -1.62; (minor set) 134.87, 117.81, 32.14, 31.84, 27.90, 26.82, 22.76, 18.52, 14.13, -1.02; MS, m/e 270 (M^+), 214, 197. 73.

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